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Modern Friedel-Crafts chemistry XIII. Intra- and intermolecular cyclization of some carbonyl derivatives under Friedel-Crafts conditions

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Carbonyl group deactivation in the cycloalkylation of aryl haloalkyl ketones was studied. Ketones **1-5** were prepared and subjected to treatment with $AlCl_3$, $AlCl_3/H_2SO_4$ and H_2SO_4 catalysts. Whereas $AlCl_3$ catalyst gave no cyclization products, the use of $AlCl_3/H_2SO_4$ and H_2SO_4 catalysts afforded the corresponding indanones and/or tetralones (**6-11**). The intermediate p-methylacrylophenone (**12**) was also obtained in the case of ketone **2**.

Furthermore, intermolecular cyclizations of benzene, toluene and p-xylene with 3-chloropropionyl chloride (**13**) and 4-chlorobutyryl chloride (**14**) were investigated. In the presence of $AlCl_3/CH_3NO_2$ catalyst, only the corresponding aryl haloalkyl ketones (**1-5**) were formed whereas the use of $AlCl_3$ catalyst gave, in addition, some cyclic ketones. However, the use of $AlCl_3/H_2SO_4$ catalyst gave only the corresponding cyclic ketones (**6-11**).

Results are discussed and mechanisms are suggested. In conclusion, carbonyl group deactivation for ring closure is demonstrated in the investigated ketones and cyclization can only effected under strenuous conditions.

Résumé. — La cycloalkylation des aryl haloalkyl cétones a été étudiée. Les cétones **1-5** ont été préparées et traitées avec les catalyseurs $AlCl_3$, $AlCl_3/H_2SO_4$ et H_2SO_4. Alors que $AlCl_3$ ne donne pas de produits cyclisés, l'emploi de $AlCl_3/H_2SO_4$ ou H_2SO_4 conduit aux indanones et/ou aux tétralones **6-11**. La p-méthylacrylophénone **12** est aussi obtenue dans le cas de la cétone **2**.

La cyclisation intermoléculaire du benzène toluène et p-xylène avec le chlorure de chloro-3 propionyle a été étudiée. En présence de $AlCl_3/CH_3NO_2$, seules les aryl haloalkyl cétones **1-5** sont formées, alors qu'avec $AlCl_3$, on observe un peu de cétones cycliques. Par contre, l'utilisation de $AlCl_3/H_2SO_4$ donne uniquement les cétones cycliques **6-11**.

Les résultats sont discutés et des mécanismes sont proposés.

Introduction

The cycloalkylation of aryl haloalkyl ketones has a special significance from the mechanistic and synthetic points of views. Inspection of previous results revealed considerable discrepancies (1-17). Some authors indicated that such cycloalkylation reactions could only be effected under strenuous conditions (3, 5, 9, 11) while others reported facile ring closure to the corresponding indanone or tetralone derivatives (1, 2). Recently, Pines and Douglas (14) showed, using isotopic labelling, that the closure of these compounds proceeded *via* the intermediate aryl alkenyl ketones. In view of these discrepancies and of the fact that aromatic carbonyl compounds have low reactivity towards electrophilic substitution reactions (9, 11, 18, 21) we decided to tackle this problem in the ensuing discussion. The results are compared to those from earlier studies and discussed in terms of our recent findings about ring closure reactions (11, 22, 31).

Results and discussion

The starting aryl haloalkyl ketones, 3-chloropropiophenone (**1**) ; 4'-methyl-3-chloropropiophenone (**2**) ; 2'-5'-dimethyl-3-chloropropiophenone (**3**) ; 4-chlorobutyrophenone (**4**) and 2',5'-dimethyl-4-chlorobutyrophenone (**5**) were prepared *via* interaction of 3-chloropropionyl chloride (**13**) and 4-chlorobutyryl chloride (**14**) with the corresponding diarylcadmium (**32**) and their cycloalkylation reactions were examined in the presence of different Friedel-Crafts catalysts such as $AlCl_3$, $AlCl_3/H_2SO_4$ and H_2SO_4.

Surveying the results of table 1 showed that in the presence of $AlCl_3$ catalyst ketones **1-5** were recovered unchanged even when we used more than two folds of $AlCl_3$ (1:2.4) whereas in the presence of either $AlCl_3/H_2SO_4$ or H_2SO_4 catalysts **1-4** gave the corresponding indanone derivatives (**6-9**), respectively. In the case of **2**, we also obtained p-methylacrylophenone (**12**) in addition to **7**. Ketone **5** gave under similar conditions a mixture of 3,4,7-trimethyl-1-indanone (**10**) and 5,8-dimethyl-1-tetralone (**11**).

As suggested by Pines and Douglas (14), the ring closure of aryl chloroalkyl ketones (**1-5**) in the presence of H_2SO_4 or $AlCl_3/H_2SO_4$ catalysts could be assumed to occur *via* the intermediates aryl alkenyl ketones which are formed through HCl elimination of the enol forms of ketones **1-5**, as shown in the case of **2**, in scheme 2. Of course, the isolation of **12** during the cycloalkylation of **2** with $AlCl_3/H_2SO_4$ and H_2SO_4 catalysts supports this view (table 1, entries 5, 6). The cycloalkylation of aryl alkenyl ketones was studied by us in a previous manuscript (31). The formation of **11**, however, upon cycloalkylation of **5** (table 1, entries 14, 15) could be ascribed to the higher reactivity of the xylene nucleus toward Friedel-Crafts alkylations (33), i.e. the two methyl groups in the xylene moiety in **5** compensated the carbonyl group deactivation which stabilizes the intermediate complex making cycloalkylation of **16** possible. Furthermore, the formation of benzene and toluene could be easily interpreted on the basis of the deacylation of **1** and **2**, respectively.

It is now clear that the Friedel-Crafts cycloalkylation reactions of aryl chloroalkyl ketones, as well as other electrophilic substitution, are supressed by the presence of carbonyl group directly connected to the aromatic ring. This is understandable on the basis of the possibility of coordination with acid catalysts ($C=\dot{O}:A\bar{l}Cl_3$ or $C=\dot{O}:H$) and/or the formation of stable oxonium ions similar to those detected by Pines and Douglas (14).

To further clarify this problem, this work was extended to the intermolecular cyclization of some arenes such as benzene, toluene and p-xylene with 3-chloropropionyl chloride (**13**) and with 4-chlorobutyryl chloride (**14**) under the same previous

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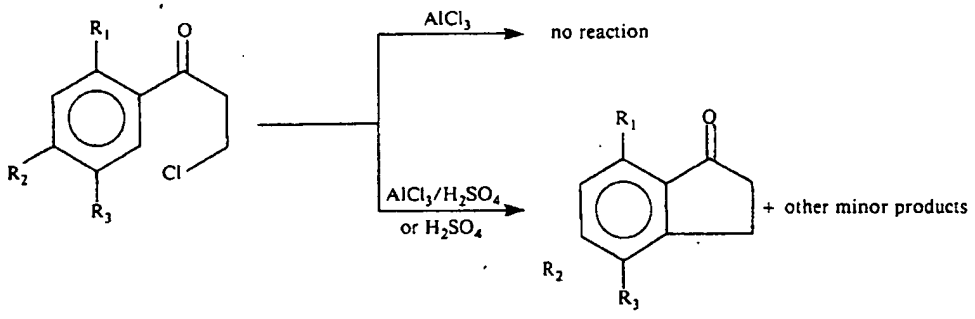
TABLE I

Reaction of aryl chloroalkyl ketones with Friedel-Crafts catalysts

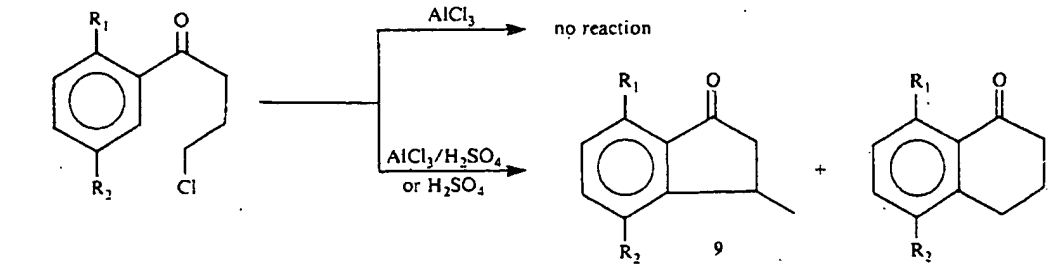
Entry No.	Starting ketone	Reaction conditions				Reaction products (%)
		Catalyst	Solvent	Temp. (°C)	Time (hrs)	
1	3-chloropropiophenone	$AlCl_3$	CS_2	RT	3	Recovered starting material (94)
2	"	$AlCl_3/H_2SO_4$	"	25-90	4	1-indanone (60) ; benzene (trace)
3	"	H_2SO_4	—	90	1	1-indanone (80)
4	4'-methyl-3-chloropropiophenone	$AlCl_3$	CS_2	RT	3	Recovered starting material (95)
5	"	$AlCl_3/H_2SO_4$	"	25-90	4	5-methyl-1-indanone (75) ; p-methylacrylophenone (5) ; toluene (trace)
6	"	H_2SO_4	—	90	1	5-methyl-1-indanone (76) ; p-methylacrylophenone (5) ; toluene (trace)
7	2',5'-dimethyl-3-chloropropiophenone	$AlCl_3$	CS_2	RT	3	Recovered starting material (90)
8	"	$AlCl_3/H_2SO_4$	"	25-90	4	4,7-dimethyl-1-indanone (81)
9	"	H_2SO_4	—	90	1	4,7-dimethyl-1-indanone (90)
10	4-chlorobutyrophenone	$AlCl_3$	CS_2	RT	3	Recovered starting material (90)
11	"	$AlCl_3/H_2SO_4$	"	25-90	4	3-methyl-1-indanone (68)
12	"	H_2SO_4	—	90	1	3-methyl-1-indanone (70)
13*	2',5'-dimethyl-4-chlorobutyrophenone	$AlCl_3$	CS_2	RT	3	Recovered starting material (85)
14	"	$AlCl_3/H_2SO_4$	"	25-90	4	3,4,7-trimethyl-1-indanone (50) ; 5,8-dimethyl-1-tetralone (20)
15	"	H_2SO_4	—	90	1	3,4,7-trimethyl-1-indanone (55) ; 5,8-dimethyl-1-tetralone (16)

(*) This experiment was repeated using 0.024 mole of $AlCl_3$ for 0.01 mole of 2,5-dimethyl-4-chlorobutyrophenone (5) and the starting 5 was recovered unreacted in 90%.



1, $R_1=R_2=R_3=H$
2, $R_1=R_3=H$, $R_2=CH_3$
3, $R_1=R_3=CH_3$, $R_2=H$

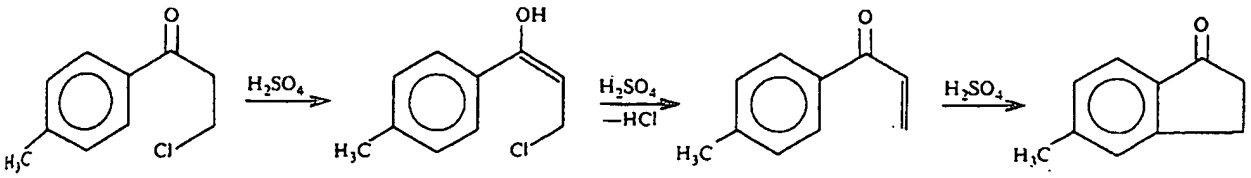
6
7
8



4, $R_1=R_2=H$
5, $R_1=R_2=CH_3$

9
10
11

Scheme I



2 enolic form 12 7

Scheme 2

TABLE 2

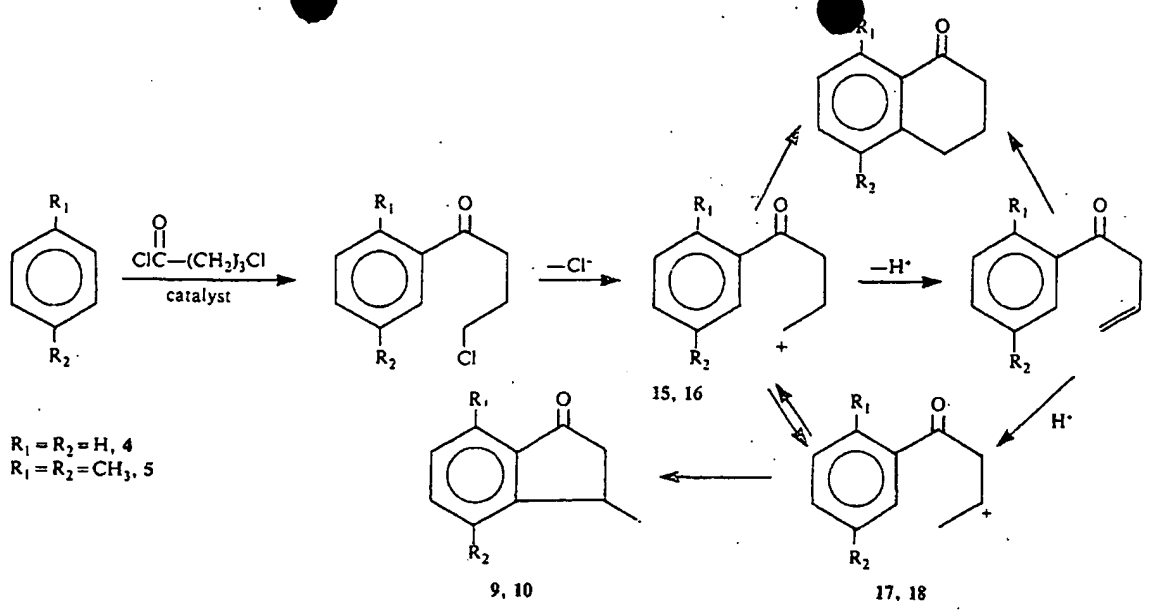
Reactions of haloacid chlorides with arenes in the presence of Friedel-Crafts catalysts

Entry No.	Arene	Haloacid chloride	Reaction conditions				Reaction products (%)
			Catalyst	Solvent	Temp. (°C)	Time (hrs)	
1	Benzene	3-chloropropionyl chloride	$AlCl_3/CH_3NO_2$	CS_2	RT	2	3-chloropropiophenone (88)
2	"	"	$AlCl_3$	"	RT	2	3-chloropropiophenone (71)
3	"	"	$AlCl_3/H_2SO_4$	"	25-90	4	1-indanone (58)
4	Toluene	"	$AlCl_3/CH_3NO_2$	"	RT	2	4'-methyl-3-chloropropiophenone (98)
5	"	"	$AlCl_3$	"	RT	2	4'-methyl-3-chloropropiophenone (87)
6	"	"	$AlCl_3/H_2SO_4$	"	25-90	4	5-methyl-1-indanone (60)
7	p-xylene	"	$AlCl_3/CH_3NO_2$	"	RT	2	2',5'-dimethyl-3-chloropropiophenone (97)
8	"	"	$AlCl_3$	"	RT	2	2',5'-dimethyl-3-chloropropiophenone (85)
9	"	"	$AlCl_3/H_2SO_4$	"	25-90	4	4,7-dimethyl-1-indanone (75)
10	Benzene	4-chlorobutyryl chloride	$AlCl_3/CH_3NO_2$	"	RT	2	4-chlorobutyrophenone (71)
11	"	"	$AlCl_3$	"	RT	2	4-chlorobutyrophenone (55) ; 3-methyl-1-indanone (25)
12	"	"	$AlCl_3/H_2SO_4$	"	25-90	4	3-methyl-1-indanone (70)
13	p-xylene	"	$AlCl_3/CH_3NO_2$	"	RT	2	2',5'-dimethyl-4-chlorobutyrophenone (85)
14	"	"	$AlCl_3$	"	RT	2	2',5'-dimethyl-4-chlorobutyrophenone (48) ; 3,4,7-trimethyl-1-indanone (25) ; 5,8-dimethyl-1-tetralone (10)
15	"	"	$AlCl_3/H_2SO_4$	"	25-90	4	3,4,7-trimethyl-1-indanone (48) ; 5,8-dimethyl-1-tetralone (33)

conditions. Formerly, intermolecular cyclization of arenes with bifunctional molecules has found little attention (16, 33, 36). In the present work, in the presence of the mild $AlCl_3/CH_3NO_2$ catalyst, the interaction of **13** and **14** with benzene, toluene and p-xylene gave only the corresponding aryl haloalkyl ketones, no cyclization products could be detected (table 2, entries 1, 4, 7, 10, 13). These ketones (**1-5**) were identical in all respects to those obtained *via* the alternative method (32) and therefore this method has a considerable synthetic value. With the strong $AlCl_3$ catalyst, **13** again interacted with benzene, toluene and p-xylene but gave no cyclization products (table 2, entries 2, 5, 8). With the latter strong catalyst, however, **14** interacted with benzene and p-xylene to give a product mixture in which the cyclic ketones were observed (table 2, entries 11, 14). The formation of **9** and **10** may be attributed to the possible rearrangement of the initially formed primary carbocations (**15** and **16**), while the formation of the **11** is due to the direct attack of **16** on the reactive p-xylene moiety (scheme 3). On the other hand, this reaction was tested using $AlCl_3/H_2SO_4$ catalyst. Under these conditions **13** gave, upon interaction with benzene, toluene and p-xylene, 1-indanone (**6**, 58%), 5-methyl-1-indanone (**7**, 60%) and 4,7-dimethyl-1-indanone (**8**, 75%), respectively. With **14** benzene gave entirely, under the former conditions, the rearrangement product 3-methyl-1-indanone (**9**, 68%) and non of the direct closure product, 1-tetralone (**19**), could be detected. This indicates that rearrangement of the **15** to **17** was complete prior to the closure step in this case. Furthermore, attempted isomerization of **10** to **11** and vice versa was carried out using $AlCl_3/H_2SO_4$ catalyst and pure samples of each **10** and **11** under the same reaction conditions. However, the starting **10** (or 11) was recovered unchanged and the other isomer **11** (or **10**), respectively, could not be detected. These results show that the indanone **10** and the tetralone **11** are primary, but not rearranged, products.

5,8-dimethyl-1-tetralone (**11**, 23%) was formed, in addition to 3,4,7-trimethyl-1-indanone (**10**, 44%) during the reaction of **14** with p-xylene under the same catalytic conditions. The production of **11** is, of course, due to the compensation of the carbonyl deactivation by the two methyl groups which made the closure of the primary carbocation (**16**) possible (23).

The identities of the products were confirmed by matching all physical properties and spectroscopic data with known samples.



Scheme 3

Experimental

All melting points were determined using a Kofler melting point apparatus and were uncorrected. A Pye-Unicam gas chromatograph series 105 was used for GLC analysis using 5' × $\frac{1''}{8}$ column packed with 10% SE 30 over chromosorb and nitrogen flow rate 60 ml/min. Isolation of products was also achieved using 100 × 2 cm glass column packed with thin silica gel film. The ir spectra were obtained on a Pye-Unicam SP 200 G spectrophotometer.

Starting materials

The aryl chloroalkyl ketones (1-5) were prepared *via* interaction of 3-chloropropionyl chloride (13) or 4-chlorobutyryl chloride (14) with the proper diarylcadmium according to the procedure of Cason (32). For example, reaction of 13 with diphenylcadmium, di-p-toly-1-cadmium, and with di(p-xylyl) cadmium gave 3-chloropropiophenone (37) (1, 51%), 4'-methyl-3-chloropropiophenone (38) (2, 61%) and 2',5'-dimethyl-3-chloropropiophenone (4) (3, 42%), respectively. Also, 4-chlorobutyrophenone (39) (4, 50%) and 2',5'-dimethyl-4-chlorobutyrophenone (40) (5, 40%) were prepared *via* interaction of 14 with diphenylcadmium and di(p-xylyl) cadmium, respectively. The prepared materials (1-5) gave correct elemental and spectral data as well as the same literature boiling (or melting) points.

Authentic samples

• *1-indanone* (6) :

Treatment of 3-phenylpropionyl chloride (9 g, 0.06 mole) with $AlCl_3$ (10 g, 0.075 mole) in 100 ml CS_2 with reflux for three hours gave 5 g (78%) of 6, mp 40°C, lit. (16) 40-1°C.

• *5-methyl-1-indanone* (7) :

Reaction of 3-(p-tolyl)propionyl chloride with $AlCl_3$ as described above gave 7 in 35% yield, mp 71°C, lit. (41) mp 71°C.

• *4,7-dimethyl-1-indanone* (8) :

3-(p-xylyl) propionic acid was prepared as described earlier (42) from 2,5-dimethyl (propiophenone, sulfur and morpholine in 53% yield, mp 132°C, lit. (43) mp 131°C. 3-(p-xylyl) propionyl chloride (5 g; 0.025 mole ; prepared by refluxing the acid with $SoCl_2$ in benzene) was refluxed for six hours with $AlCl_3$ (3.7 g, 0.028 mole) in 100 ml CS_2. The product (8, 2.5 g, 61%) was melted at 76°C (methanol), lit. (4) mp 76-77°C.

• *3-methyl-1-indanone* (9) :

3-phenylbutyric acid, previously prepared from benzene and crotonic acid in the presence of $AlCl_3$ and HCl gas (44), was converted to 3-phenylbutyryl chloride with PCl_3. The latter (5.4 g, 0.3 mole) was treated with $AlCl_3$ (5.3 g, 0.04 mole) in 10 ml nitromethane for three hours to yield 3-methyl-1-indanone (9, 4.39 g, 90%), bp 118°C/11 mmHg, lit. (45). 118°C/11 mmHg.

• *3,4,7-trimethyl-1-indanone* (10) :

Crotonic acid (8.69, 0.1 mole) and p-xylene (10.6 g, 0.1 mole) gave upon treatment with $AlCl_3$ in CS_2 as described before, the target compound 10 (12 g, 68%), mp 32°C, lit. (46) mp 31-32°C.

• *5,8-dimethyl-1-tetralone* (11) :

3-(2,5-dimethylbenzoyl) propionic acid, prepared by reacting of p-xylene (26 g, 0.25 mole) and succinic anhydride (25 g, 0.25 mole) with $AlCl_3$ (40.1 g, 0.3 mole) in 200 ml CS_2 [35 g, 69%, mp 86°C, lit. (47) 86°C], was reduced to 4-(p-xylyl)butyric acid [68%, mp 70°C, lit. (48) mp 71°C] using hydrazine hydrate in diethylene glycol (49). The corresponding acid chloride, obtained through reflux of the acid with thionyl chloride in benzene, was treated with $AlCl_3$ in CS_2 under reflux condition for two hours. The product was 11 (68%), mp 32°C, lit. (47) 33°C.

Intramolecular cyclization (general procedures)

The following general procedures were carried out during the present work.

A) Reaction of aryl haloalkyl ketones with $AlCl_3$ catalyst :

A solution of 0.01 mole aryl haloalkyl ketone in 25 ml CS_2 was added to a mixture of 0.012 mole $AlCl_3$ and 50 ml CS_2 contained in two necked flask equipped with a reflux condenser capped with calcium chloride tube, a magnetic stirrer and a dropping funnel. In all runs, unless otherwise stated, the reaction mixture was stirred for three hours at room temperature (RT), decomposed with 10% HCl solution, extracted with ether and the ether extract was washed with water, 10% sodium carbonate solution, again with water and dried over magnesium sulfate. The solvents, ether and CS_2, were removed by distillation and the residue was identified as described under each individual run. Results are found in table 1.

B) Reaction of aryl haloalkyl ketones with $AlCl_3/H_2SO_4$ catalyst :

As in method A, a solution of 0.01 mole of aryl haloalkyl ketone in 50 ml CS_2 was added to 0.012 mole $AlCl_3$ in 25 ml CS_2 and the

mixture was stirred for three hours, the CS_2 was removed under reduced pressure and then 10 ml of conc. H_2SO_4 was added to the oily residue. The reaction mixture was heated for one hour at 90°C, cooled to room temperature, diluted with water, extracted with ether and the ether extract was treated as above. Results are described under each individual run.

C) Reaction of aryl haloalkyl ketones with H_2SO_4 catalysts :

A mixture of aryl haloalkyl ketone (0.01 mole) and conc. H_2SO_4 (10 ml) was heated at 90°C while stirring for one hour, cooled, diluted with water and the product separated as described before. Separation and identification of the products are discussed under each individual experiment.

Reaction of 3-chloropropiophenone (1) *with $AlCl_3$ catalyst :*

A solution of 1 (1.6 g, 0.01 mole) in 25 ml CS_2 was treated with $AlCl_3$ (1.6 g, 0.012 mole) as described before. The starting ketone (1, 1.5 g, 94%) was recovered (table 1, entry 1).

o Reaction of 1 with $AlCl_3/H_2SO_4$ catalyst : as described in the general procedure, 1, 1.6 g, 0.01 mole) gave after treatment with $AlCl_3/H_2SO_4$ catalyst, 1-indanone (6, 0.8, 60%) and a trace of benzene (table 1, entry 2).

o Reaction of 1 with H_2SO_4 catalyst : a sample of 1 (1.6 g, 0.01 mole) was treated with 10 ml conc. H_2SO_4. GIC analysis showed only single peak at the same retention time as authentic sample of 1-indanone (6, 1 g, 82%), table 1, entry 3.

o Reaction of 4'-methyl-3-chloropropiophenone (2) with $AlCl_3$ catalyst : starting with 2 (1.8 g, 0.01 mole) and $AlCl_3$ (1.6 g, 0.012 mole), the reaction product was 1.7 g (94%) of the starting material (table 1, entry 4).

o Reaction of 2 with $AlCl_3/H_2SO_4$ catalyst : interaction of 2 (1.8 g, 0.01 mole) with $AlCl_3/H_2SO_4$ catalyst gave 1.2 g of crude product. GLC analysis revealed three peaks corresponding to, using authentic samples, toluene (trace) ; 4-methylacrylophenone (12, 5%) and 5-methyl-1-indanone (7, 75%), mp and mmp 70°C, lit. (41) mp 70°C (table 1, entry 5).

o Reaction of 2 with H_2SO_4 catalyst : a sample of 2 (1.8 g, 0.01 mole) was treated with 10 ml conc. H_2SO_4. GLC analysis of the crude product, using authentic samples, revealed two peaks for 4-methylacrylophenone (12, 5%) and 5-methyl-1-indanone (7, 92%). Also, GLC/mass spectrometric analysis showed a parent ion of m/z 147 with fragmentation pattern in accord with the structure of 7 (table 1, entry 6).

o Reaction of 2',5'-dimethyl-3-chloropropiophenone (3) with $AlCl_3$ catalyst : a solution of 3 (2.0 g, 0.01 mole) in CS_2 was treated with $AlCl_3$ (1.6 g, 0.012 mole) as described above. The product was 1.8 g (90%) of the starting ketone (table 1, entry 7).

o Reaction of 3 with $AlCl_3/H_2SO_4$ catalyst : treatment of 3 (2.09, 0.01 mole) with $AlCl_3/H_2SO_4$ catalyst gave 4,7-dimethyl-1-indanone (8, 1.3 g, 81%), mp and mmp 76°C, lit. (4) mp 77°C (table 1, entry 8).

o Reaction of 3 with H_2SO_4 catalyst : a sample of 3 (2 g, 0.01 mole) gave after treatment with H_2SO_4 catalyst 4,7-dimethyl-1-indanone 8 (1.4 g, 90%) ; mp, mmp 77°C, lit. (4) mp 77°C (table 1, entry 9).

o Reaction of 4-chlorobutyrophenone (4) with $AlCl_3$ catalyst : treatment of 4 (1.8 g, 0.01 mole) with $AlCl_3$ (1.6 g, 0.017 mole) in CS_2 gave no cyclization products and the starting ketone 4 was recovered (1.6 g, 88%) ; table 1, entry 10.

o Reaction of 4 with $AlCl_3/H_2SO_4$ catalyst : interaction of 4 (1.8 g, 0.01 mole) with $AlCl_3/H_2SO_4$, as in the general procedure, gave 1 g of crude product identified by GLC technique using an authentic sample as 3-methyl-1-indanone (9,68%) ; table 1, entry 11.

o Reaction of 4 with H_2SO_4 catalyst : a mixture of 4 (1.8 g, 0.01 mole) in 10 ml conc. H_2SO_4 was allowed to react as described earlier. The product was 3-methyl-1-indanone (9, 19,68%) identified as above (table 1, entry 12).

o Reaction of 2',5'-dimethyl-4-chlorobutyrophenone (5) with $AlCl_3$ catalyst : treatment of 5 (2.1 g, 0.01 mole), with $AlCl_3$ (1.6 g, 0.012 mole) in CS_2 gave no cyclization products and the starting material (5) was recovered (1.75 g, 85%) ; this experiment was repeated using 2.1 g (0.01 mole) of 5 for 3.24 g (0.024 mole) of $AlCl_3$. Also, the starting 5 was recovered unchanged (1.99, 90%), table 1, entry 13.

o Reaction of 5 with $AlCl_3/H_2SO_4$ catalyst : a sample of 5 (2.1 g, 0.01 mole) was treated with $AlCl_3/H_2SO_4$ catalyst. The product was found to be, using GLC technique and authentic samples, a mixture of 3,4,7-trimethyl-1-indanone (10, 50%) and 5,8-dimethyl-1-tetralone (11, 20%) ; table 1, entry 14.

o Reaction of 5 with H_2SO_4 catalyst : interaction of 5 (2.1 g, 0.01 Mole) with 10 ml conc. H_2SO_4 resulted in the formation of a mixture of 3,4,7-trimethyl-1-indanone (10, 53%) and 5,8-dimethyl-tetralone (11, 16%) ; table 1, entry 15.

Attempted isomerization of 3,4,7-trimethyl-1-indanone (10) *and 5,8-dimethyl-1-tetralone* (11) *with $AlCl_3/H_2SO_4$ catalyst :*

A solution of 10 (1.74 g, 0.01 mole) in 25 ml CS_2 was treated with $AlCl_3$ (1.62 g, 0.012 mole) in 50 ml CS_2 in the presence of 5 ml conc. H_2SO_4 as described above. The starting 10 was recovered in 92% yield (1.6 g).

Treatment of 11 (1.74 g, 0.01 mole) with the same catalyst under the same conditions afforded only unreacted 11 (1.5 g, 86.2%).

INTERMOLECULAR CYCLIZATION (GENERAL PROCEDURES)

Three different techniques were followed during the progress of this work.

A) Reaction of haloacid chlorides with arenes in the presence of $AlCl_3/CH_3NO_2$ catalyst :

To a mixture of 0.12 mole of $AlCl_3$ in 50 ml CS_2 placed in two necked flask, 0.12 mole of nitromethane was added slowly while stirring. After stirring for one hour, 0.1 mole of the arene was added followed by the addition of 0.1 mole of the haloacid chloride over a period of one hour. The reaction mixture was stirred for an additional two hours at room temperature, decomposed and extracted as in the case of the reactions of aryl haloalkyl ketones with $AlCl_3$ catalyst. Separation and identification of the reaction products are described under each individual run. Results are found in table 2.

B) Reaction of haloacid chlorides with arenes in the presence of $AlCl_3$ catalyst :

A two necked flask was charged with 0.12 mole $AlCl_3$ and 50 ml dry CS_2. To this mixture, was added 0.1 mole of the arene followed by dropwise addition of 0.1 mole of the haloacid chloride during one hour with stirring. The reaction mixture was treated as discussed before and identification of the products is described for each case. Results are tabulated in table 2.

C) Reaction of haloacid chlorides with arenes in the presence of $AlCl_3/H_2SO_4$ catalyst :

A solution of 0.05 mole of the arene and 0.05 mole of the haloacid chloride in 25 ml CS_2 was added during one hour while stirring to a mixture of 0.06 mole $AlCl_3$ in 50 ml CS_2 contained in two necked flask. After stirring for three hours at room temperature, the solvent was removed under vacuum and 10 ml of conc. H_2SO_4 was slowly added to the oily residue. After heating for one hour at 90°C, the reaction mixture was cooled to room temperature, decomposed and extracted as usual. Results are presented in table 2.

o Reaction of benzene with 3-chloropropionyl chloride (13) in the presence of $AlCl_3/CH_3NO_2$ catalyst : benzene (7.8 g, 0.1 mole) was treated with 13 (12.7 g, 0.1 mole) in the presence of $AlCl_3/CH_3NO_2$ catalyst (0.11 mole), prepared from $AlCl_3$ (14.5 g, 0.12 mole) and nitromethane (7.3 g, 0.12 mole). The reaction mixture was processed according to the former general procedure. The product was 3-chloropropiophenone (1, 15 g, 88.5%) ; mp, mmp 48°C, lit. (37) mp 49°C (table 2, entry 1).

o Reaction of benzene with 13 in the presence of $AlCl_3$ catalyst : the reaction of benzene (7.8 g, 0.1 mole) with 13 (12.7 g, 0.1 mole) in the presence of $AlCl_3$ catalyst (16.2 g, 0.12 mole) as in the procedure mentioned above gave 3-chloropropiophenone (1, 12 g, 71%) ; mp, mmp 49°C, lit. (37) mp 49°C (table 2, entry 2).

o Reaction of benzene with 13 in the presence of $AlCl_3/H_2SO_4$: a mixture of benzene (7.8 g, 0.1 mole) and 13 (12.7 g, 0.1 mole) was treated with $AlCl_3$ (16.2 g, 0.12 mole) and 10 ml of conc. H_2SO_4 as described before. The product was identified, using authentic sample and GLC technique, as 1-indanone (6, 7 g, 58%) ; table 2, entry 3.

o Reaction of toluene with **13** in the presence of $AlCl_3/CH_3NO_2$ catalyst : reaction of toluene (9.2 g, 0.1 mole) with **13** (12.7 g, 0.1 mole) in the presence of $AlCl_3/CH_3NO_2$ catalyst (0.12 mole) gave 4'-methyl-3-chloropropiophenone (**2**, 18 g, 98%) ; mp, mmp 77°C, lit. (38) mp 75-76°C (table 2, entry 4).

o Reaction of toluene **13** in the presence of $AlCl_3$ catalyst : toluene (9.2 g, 0.1 mole) was allowed to react with **13** (12.7 g, 0.1 mole) in the presence of $AlCl_3$ catalyst as described before. The product was 4'-methyl-3-chloropropiophenone (**2**, 16 g, 87%) ; mp, mmp 77°C, lit. (38) mp 75-76°C (table 2, entry 5).

o Reaction of toluene with **13** in the presence of $AlCl_3/H_2SO_4$ catalyst : a solution of toluene (9.2 g, 0.1 mole) and **13** (12.7 g, 0.1 mole) was treated with $AlCl_3$ (16.2 g, 0.12 mole) and H_2SO_4 (10 ml) as in the general procedure. The crude product (9 g) showed a single peak in GLC analysis corresponding to, using an authentic sample, 5-methyl-1-indanone (**7**, 60%) ; table 2, entry 6.

o Reaction of p-xylene with **13** in the presence of $AlCl_3/CH_3NO_2$ catalyst : interaction of p-xylene (10.6 g, 0.1 mole) with **13** (12.7 g, 0.1 mole) in the presence of $AlCl_3/CH_3NO_2$ catalysts (0.12 mole) gave 2'-5'-dimethyl-3-chloropropiophenone (**3**, 19.5 g, 98%) ; mp, mmp 79°C, lit. (38) mp 80°C (table 2, entry 7).

o Reaction of p-xylene with **13** in the presence of $AlCl_3$ catalyst : treatment of a mixture of p-xylene (10.6 g, 0.1 mole) and **13** (12.7 g, 0.1 mole) with $AlCl_3$ (16.2 g, 0.12 mole) in 100 ml CS_2 gave 2'-5'-dimethyl-3-chloropropiophenone (**3**, 18 g, 85%) ; mp, mmp 80°C, lit. (4, 38) mp 80°C (table 2, entry 8).

o Reaction of p-xylene with **13** in the presence of $AlCl_3/H_2SO_4$ catalyst : p-xylene (10.6 g, 0.1 mole) was treated with **13** (12.7 g, 0.1 mole) in the presence of $AlCl_3/H_2SO_4$ catalyst. The product was identified by GLC, using an authentic sample, as 4,7-dimethyl-1-indanone (**8**, 12,75%) ; mp, mmp 77°C, lit. (16) mp 77°C (table 2, entry 9).

o Reaction of benzene with 4-chlorobutyryl chloride (**14**) in the presence of $AlCl_3/CH_3NO_2$ catalyst : benzene (7.8 g, 0.1 mole) and **14** (14.1 g, 0.1 mole) reacted in the presence of $AlCl_3/CH_3NO_2$ (0.12 mole) catalyst to give 4-chlorobutyrophenone (**4**, 14.5 g, 71%), bp 125°C/5 mmHg, lit. (39) 126-129°C/5 mmHg (table 2, entry 10).

o Reaction of benzene with **14** in the presence of $AlCl_3$ catalyst : a mixture of benzene (7.8 g, 0.1 mole), **14** (14.1 g, 0.1 mole) and $AlCl_3$ (16.2 g, 0.1 mole) in 100 CS_2 was reacted as mentioned before. The product was found, using GLC and authentic samples, to be a mixture of 4-chlorobutyrophenone (**4**, 55%) and 3-methyl-1-indanone (**9**, 25%) ; table 2, entry 11).

o Reaction of benzene with **14** in the presence of $AlCl_3/H_2SO_4$ catalyst : **14** (16.1 g, 0.1 mole) and benzene (7.8 g, 0.1 mole) reacted in the presence of $AlCl_3/H_2SO_4$ catalyst. TLC and GLC analysis, using authentic sample, showed that the product is 3-methyl-1-indanone (**9**, 10 g, 69%) ; table 2, entry 12.

o Reaction of p-xylene with **14** in the presence of $AlCl_3/CH_3NO_2$ catalyst : reaction of p-xylene (10.6 g, 0.1 mole) with **14** (14.1 g, 0.1 mole) in the presence of $AlCl_3/CH_3NO_2$ catalyst (0.12 mole) afforded 2',5'-dimethyl-4-chlorobutyrophenone (**5**, 18 g, 85%), bp 146-148°C/7 mmHg, lit. (40) ; bp 142-148°C/7 mmHg (table 2, entry 13).

o Reaction of p-xylene with **14** in the presence of $AlCl_3$ catalyst : the reaction of p-xylene (10.6 g, 0.1 mole) with **14** (14.1 g, 0.1 mole) in the presence of $AlCl_3/CH_3NO_2$ catalyst (0.12 mole) afforded 2',5'-dimethyl-4-chlorobutyrophenone (**5**, 18 g, 85%), bp 146-148°C/7 mmHg, lit. (40) ; bp 142-148°C/7 mmHg (table 2, entry 13).

o Reaction of p-xylene with **14** in the presence of $AlCl_3$ catalyst : the reaction of p-xylene (10.6 g, 0.1 mole) with **14** (14.1 g, 0.1 mole) in the presence of $AlCl_3$ (0.12 mole) gave a product mixture consisting of using GLC and authentic samples, 2',5'-dimethyl-4-chlorobutyrophenone (**5**, 48%) ; 3,4,7-trimethyl-1-indanone (**10**, 25%) and 5,8-dimethyl-1-tetralone (**11**, 10%), table 2, entry 14.

o Reaction of p-xylene with **14** in the presence of $AlCl_3/H_2SO_4$ catalyst : a sample of p-xylene (10.6 g, 0.1 mole) was treated with **14** (14.1 g, 0.1 mole) and $AlCl_3/H_2SO_4$ catalyst according to the general procedure. The product was found to be a mixture of **10** and **11** (48%, 33%, respectively), table 2, entry 15.

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